

Geosphere-Biosphere Interactions and Climate

Edited by

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1 The Antarctic Ozone Hole, a Human-Caused Chemical Instability in the Stratosphere

What Should We Learn from It?

PAUL J. CRUTZEN

ABSTRACT

Atmospheric ozone plays a critical role in limiting the penetration of biologically harmful, solar ultraviolet radiation to the Earth surface. Furthermore, the absorption of ultraviolet radiation from the Sun and infrared radiation emitted from the Earth's warm surface influence temperatures in the lower stratosphere, creating dynamically stable conditions with strongly reduced vertical exchange. Through industrial emissions, ozone-depleting catalysts have increasingly been produced in the stratosphere, leading to reductions in ozone. The situation is especially grave during springtime over Antarctica, where, since the 1980s, each year almost all ozone in the 14–22 km height region is chemically destroyed. This so-called “ozone hole” was not predicted by any model and came as a total surprise to all scientists. The ozone hole developed at a least likely location. Through the emissions of chlorofluorocarbons, humankind has created a chemical instability, leading to rapid loss of ozone. A question is whether there may be other instabilities that might be triggered in the environment by human activities.

1.1 Introduction

The study of the chemistry of the atmosphere is both of immediate scientific interest and of high social relevance. We first note that the gases that are most significant for atmospheric chemistry and for the Earth's climate are not its main components – nitrogen (N_2), oxygen (O_2), and argon (Ar), which together with variable amounts of water vapor make up greater than 99.9% of the molecules in the Earth's atmosphere – but rather are many gases that are found only in very low concentrations. The main gases cannot be influenced significantly by human activities. The minor gases can. Several of them play important roles in climate and atmospheric chemistry. Carbon dioxide (CO_2), which currently has a concentration of approximately 360 among 1 million air molecules, is of crucial importance in that, together with water vapor and sunlight, it builds the organic molecules of living matter. Carbon dioxide is also of great significance for the Earth's climate, an important theme of this conference. However, despite these important aspects, CO_2 plays no significant direct role in atmospheric chemistry.

The chemically reactive gases have even much lower abundances in the atmosphere than CO_2 . Several of them also act as greenhouse gases. One among these is ozone (O_3),

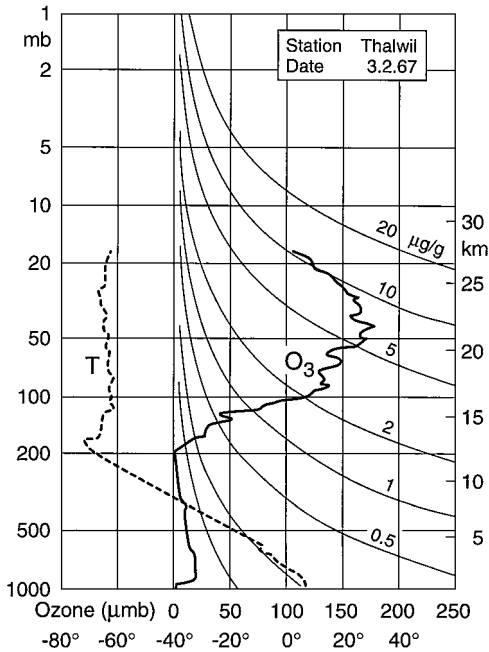


Figure 1.1. Measured ozone and temperature profiles over Thalwil, Switzerland, 1967.

which, next to water vapor, is the most important gas for the photochemistry of the atmosphere. Without ozone, the chemistry and chemical composition of the atmosphere would be totally different.

Looking at the temperature and ozone profiles of the atmosphere, as shown in Figure 1.1, we recognize that in the troposphere – that part of the atmosphere where temperatures decrease with height – ozone concentrations are quite low. Higher up, in the stratosphere, ozone concentrations rise steeply with altitude until 25–30 km, and temperatures no longer decrease. Because of this even temperature distribution with height, vertical mixing in the stratosphere is much suppressed. This is also why the stratosphere is characterized by quiet “weather.” There are also few clouds in the stratosphere; however, the exceptions are important.

The stratospheric temperature structure is directly connected to the ozone distribution. The ozone that accumulates in the stable layer of the stratosphere absorbs upwelling “warm” infrared radiation from the Earth’s surface as well as ultraviolet (UV) radiation from the Sun. The latter is the same process that largely protects life on Earth from this potentially harmful radiation. This absorption of radiation from above and below provides an important energy source for the stratosphere and explains why temperatures do not decrease with height. Ozone concentrations and temperatures in the stratosphere are very closely coupled. Stable meteorological conditions keep most ozone in the stratosphere, limiting the flow of this poisonous gas to the Earth’s surface and largely confining the hydrological cycle to the troposphere. The strong coupling of ozone and temperature in the stratosphere is in my opinion a very important property of the atmosphere that is insufficiently recognized by the climate research community.

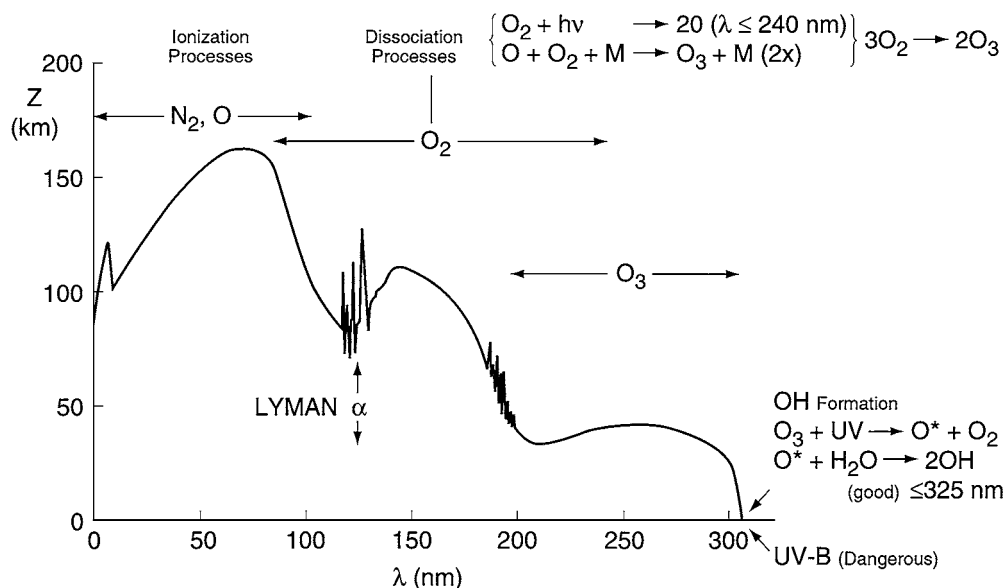
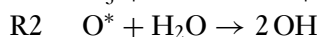
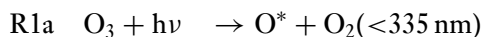


Figure 1.2. The altitude to which solar radiation penetrates into the atmosphere is a function of wavelength. Radiation shorter than 195 nm is absorbed in the mesosphere above 50 km. The longer-wavelength ultraviolet is mainly absorbed in the stratosphere by ozone.

In the troposphere there is very little ozone. Until about 20 years ago it was thought that the troposphere contained only ozone that had been transported down from the stratosphere. At that time tropospheric ozone was considered to be interesting only in the study of atmospheric transport, and its enormous importance for the chemistry of the troposphere was not recognized. Tropospheric ozone makes up only about 10% of all ozone in the atmosphere, with an average volume mixing ratio of about 40 nmol/mol (nanomole per mole, $n = \text{nano} = 10^{-9}$). However, as we discuss in this chapter, in the absence of tropospheric ozone the chemical composition of the atmosphere would be totally different.

If we look at the altitude to which solar radiation penetrates into the atmosphere, we see that the very short wavelengths – shorter than 200 nm – are to a large degree removed by 50 km (see Figure 1.2). This happens primarily through the absorption of the radiation by atomic and molecular forms of oxygen (O) and nitrogen (N). But these main gases do not absorb beyond about 240 nm. Fortunately, ozone does so very strongly in the 200–300 nm wavelength range. Were it not for atmospheric ozone, this radiation would penetrate to the Earth's surface. For the Earth's current biosphere, this would have had catastrophic consequences. Only during the past one-third of the Earth's age has the atmosphere contained comparable amounts of ozone (and oxygen) as at present. The Earth has thus been without the protective shield of oxygen and ozone during most of its existence. This must have forced primitive life to develop only in dark hideaways shielded from sun's damaging ultraviolet rays. The average concentration of ozone in the atmosphere amounts to only about 0.3 per million air molecules, but it nevertheless suffices to absorb the main part of the dangerous UV radiation.

Beyond 300 nm, the absorption ability of ozone becomes weaker so that UV radiation at longer wavelengths can penetrate to the Earth's surface. It is the radiation up to 320 nm, also called UV-B radiation (*B* stands for “biologically active”) that still poses a problem for life on Earth. Light-skinned people are all familiar with the fact that when they stay too long unprotected in the sun, they get sunburned, and from frequent exposures skin cancer may develop. Plants can also be affected by this radiation. On the other hand, we know from research conducted during the past 25 years that this same radiation is also very important for keeping our atmospheric environment clean. The reason is the following: Up to wavelengths of about 335 nm, UV radiation is capable of splitting an ozone molecule into an oxygen molecule and an excited oxygen atom (O^*). The latter has enough energy to react with atmospheric water vapor to produce hydroxyl radicals, with the chemical formula OH (Levy, 1971).



The $h\nu$ in reaction R1a, and elsewhere in this chapter, symbolizes a photon with frequency ν and energy h , where h is Planck's constant.

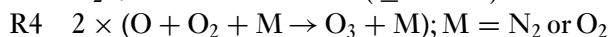
The OH radical can be called the “detergent” of the atmosphere, because it is the main species, that reacts with almost all gases, thus removing them from the atmosphere. Without OH radicals, the chemical composition of the atmosphere would be totally different.

There are three factors that are important for the formation of the OH radical: ozone, water vapor, and UV-B radiation. The average concentration of OH amounts to only about 4 out of 10^{14} air molecules (Prinn et al., 1995); negligibly few, one might say, but without this highly reactive radical the chemical composition of the atmosphere would be totally different. Molecular oxygen, which makes up almost 21% of the atmosphere, is not capable of oxidizing any of the atmospheric gases; their oxidation requires initial attack by OH radicals. Ozone in the troposphere is thus not at all the inert gas it was taken for until about 25 years ago, but rather it plays a key role in atmospheric chemistry. Although the role of ozone and hydroxyl in tropospheric chemistry is a fascinating subject, in this chapter we concentrate on stratospheric ozone.

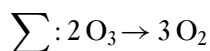
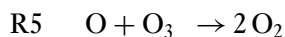
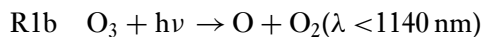
1.2 The Ozone Hole

The main part of this chapter concentrates on the topic of the stratospheric ozone and the dramatic development of the so-called “ozone hole.” To explain what has happened, I must start with a short overview of ozone layer chemistry.

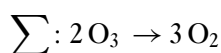
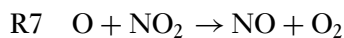
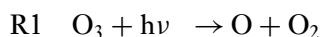
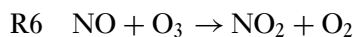
Stratospheric ozone is formed through the photolysis of oxygen by solar ultraviolet radiation of wavelengths less than 240 nm, a process that humans cannot influence. The photolysis of O_2 produces two oxygen atoms, each of which combines with oxygen molecules to form ozone (Chapman, 1930).



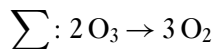
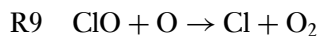
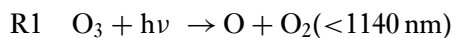
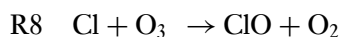
Unless there are chemical reactions going in the opposite direction, most O_2 in the atmosphere would be transformed into ozone in about 10,000 years. For many years it was thought that the return reactions from O_3 to O_2 would involve only oxygen allotropes (Chapman, 1930):



These reactions too cannot be influenced by humankind. Things changed, however, when it was realized that catalytic reactions could be more important than the previously mentioned Chapman reactions in converting O_3 back to O_2 . First, it was hypothesized by Crutzen (1970) that NO and NO_2 could catalyze the destruction of ozone:

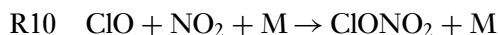


In the following year Johnston (1971) and Crutzen (1971) independently proposed that the nitric oxide emitted from the large fleets of supersonic transport aircraft, the SSTs – which were planned to be built in the United States, France, Britain, and the Soviet Union – could result in substantial ozone depletion. Only a few SSTs were ever built. However, a few years later, Molina and Rowland (1974) hypothesized that Cl and ClO, released to the atmosphere from the photochemical decay of the chlorofluorocarbon gases ($CFCl_3$ and CF_2Cl_2), could deplete ozone by a similar chain of catalytic reactions as shown earlier with NO and NO_2 :

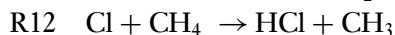


In particular, since the Second World War, the stratospheric abundance of chlorine-containing gases has increased strongly; consequently, the stratosphere now contains approximately six times more chlorine than the amount provided by methylchloride (CH_3Cl), which is emitted from the oceans. Until 1985, it was thought that ozone destruction via the ClO_x catalytic cycle would take place primarily over the altitude range 30–45 km, whereas at lower elevations, where most ozone is located, much less ozone would be destroyed. However, observations reported in 1985 by researchers of the British Antarctic Survey (Farman et al., 1985) showed that the most dramatic ozone decreases were occurring during September–October principally in the lower layers of the stratosphere over Antarctica, a finding that was totally unexpected. Previously it was believed, and this is true in most situations, that below 30 km reactions between the NO_x and ClO_x catalysts, producing hydrochloric acid (HCl) and chlorine nitrate

(ClONO₂) via



and



would strongly reduce the concentrations of the “ozone killers” NO_x and ClO_x, thus protecting ozone from otherwise much stronger destruction. Through these reactions, the majority of stratospheric inorganic chlorine is mostly tied up as HCl and ClONO₂, which do not react with O₃. That these favorable circumstances do not always exist became clear after Farman et al. (1985) discovered that average springtime (September–October) stratospheric ozone amounts above their research station Halley Bay on the Antarctic continent had been strongly decreasing year by year since the middle of the 1970s. Similar low O₃ values had also been reported by Chubachi (1984) of the Japan Polar Research Institute. From balloon soundings it became clear that rapid and complete ozone loss was taking place within a month in the same height range, 14–22 km, where maximum ozone concentrations are usually found (Figure 1.3). The observations were a total surprise to the stratospheric ozone research community. Until 1985 it had been common wisdom that the ozone in this altitude region was chemically inert. Analyses of satellite observations showed that large ozone decrease occurred over much of Antarctica during the months of September and October. The big question was, how was this possible? After only a few years of intensive research the principal causes became clear. At very cold temperatures, less than around −80 °C, which occur

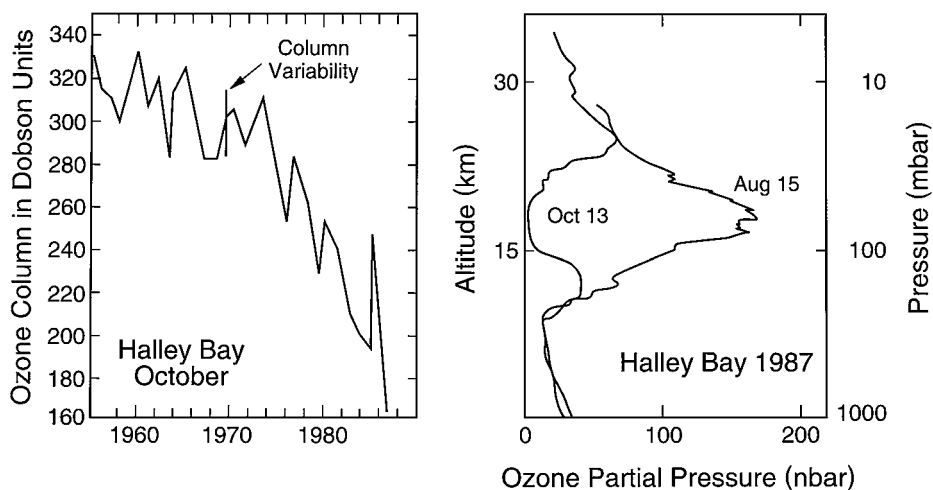
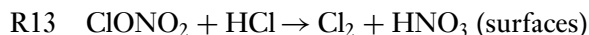
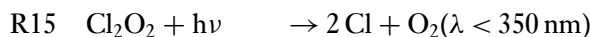
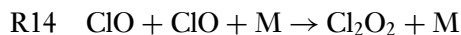
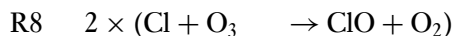


Figure 1.3. The ozone hole. The figure on the left shows the decrease in the total ozone column over the Antarctic (100 Dobson units corresponds to a layer of ozone 1 mm thick as standard temperature and pressure at the earth surface). The right-hand diagram shows the altitude dependence of ozone loss between August and October 1987. Measurements by J. Farman and coworkers of the British Antarctic Survey (1985) and by D. Hofmann and coworkers (1989) of the National Oceanic and Atmospheric Administration (NOAA) in Boulder, Colorado.

at high latitudes in the winter especially over Antarctica, condensation or sublimation of nitric acid (HNO_3) and water vapor takes place on particles (Crutzen and Arnold, 1986; Toon et al., 1986; Dye et al., 1992) that are always present in the stratosphere and that normally consist of water and sulfuric acid (H_2SO_4). This process effectively removes HNO_3 from the gas phase, and with it also the nitrogen oxides (NO and NO_2). What then happens is that HCl and ClONO_2 , the two most abundant inorganic chlorine species – which do not react with ozone or with each other in the gas phase – react in, or on the surface of, the particles to form Cl_2 and HNO_3 (Solomon et al., 1986; Molina et al., 1987; Tolbert et al., 1987):



Then, in late winter or early spring, when sunlight returns after the long polar night, the Cl_2 molecules are quickly split, producing Cl atoms. These start a very efficient catalytic chain of reactions (Molina and Molina, 1987), which results in the rapid transformation of two ozone molecules into three oxygen molecules.



The second reaction implies that the ozone destruction rate depends on the square of the ClO radical concentration. If we also consider that the formation of chemically active chlorine (Cl and ClO) by reaction R13 involves a reaction between two chlorine-containing species – ClONO_2 and HCl – we note that the rate of ozone decomposition could be proportional to between the second and fourth power of the stratospheric chlorine content. With this increasing by 4% per year, as it has been doing until the beginning of the 1990s, the ozone destruction rate could increase by between 8% and 17% per year. The current stratospheric chlorine abundance is about six times greater than that of the natural background that is provided by CH_3Cl , implying at least 36 times faster anthropogenic than natural ozone destruction by the Cl and ClO radicals. In situ observations on a stratospheric research aircraft validated the above explanation for the origin of the ozone hole (Anderson et al., 1989). Precisely in the polar areas, where the stratosphere gets very cold in winter and remains cold during early spring, measurements show high concentrations of ClO radicals and simultaneously rapid ozone destruction (Figure 1.4). It is also important to note here that because of the strong ozone loss, heating of the stratosphere in the ozone-poor air does not take place, leading to lower temperatures and thus enhancing ice or supercooled liquid particle formation, chlorine activation, and ozone depletion, producing a series of positive feedbacks.

In the meantime, it was found that also in the Northern Hemisphere during late winter and early spring, ozone is being increasingly destroyed, although to a lesser extent than over Antarctica because stratospheric temperatures are generally about 10°C higher than over Antarctica, thus causing less-efficient particle formation and chlorine activation. During the 1980s, ozone depletion was most evident between January and

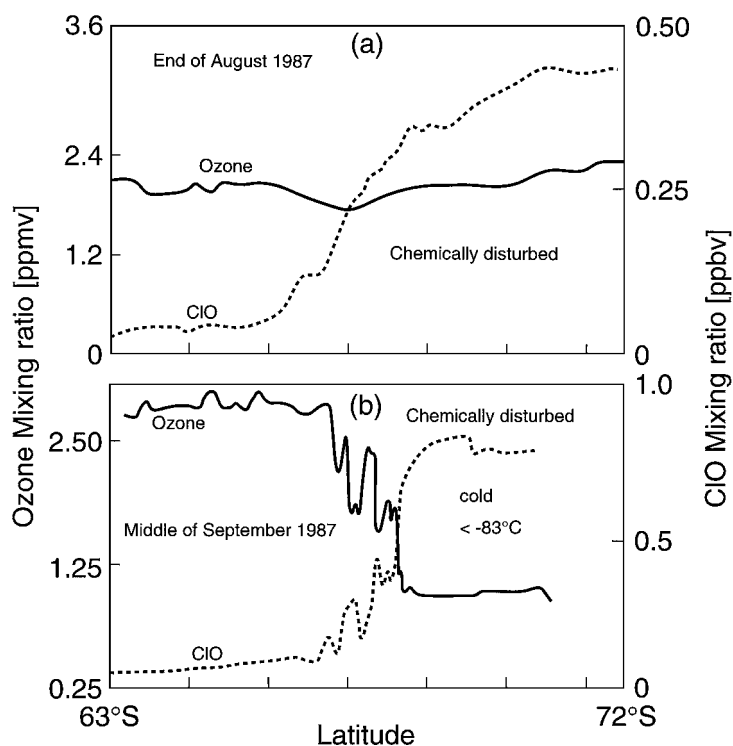


Figure 1.4. High concentrations of ClO radicals and the simultaneous rapid ozone destruction occur in winter when the temperature becomes very cold. Measurements by J. G. Anderson and coworkers (1989) of Harvard University.

April, when the destruction trend approached 1% per year. Ozone destruction took place in other seasons as well but at the lower rate of around 0.4% per year (Stolarski et al., 1991). The declining trend during winter and spring has increased during the present decade over the middle- to high-latitude zone of the Northern Hemisphere. In particular, during the winters 1995/1996 and 1996/1997 similar ozone depletions to those observed over the Antarctic about 15 years earlier were seen (e.g., Müller et al., 1997). It is therefore especially gratifying to note that since early 1986 international agreements have been in effect that forbid the production of CFCs and several other industrial Cl- and Br-containing gases in the developed world, with a decade's respite for the developing world. Hopefully this means that the damage to the ozone layer may not grow much worse in the future. However, even in the best of circumstances, full recovery of the ozone layer will be a slow process. It will take up to half a century before the ozone hole will disappear. The slowness of the repair process is due to the long average atmospheric decay times of the CFC gases, on the order of 50 years for CFC-11 and 110 years for CFC-12.

Nevertheless, as a result of these measures the worst effects on the biosphere have probably been prevented. Thus, estimates by Slaper et al. (1996) would have predicted a fourfold increase in the incidence of skin cancer during the next century if no regulatory measures had been taken. The effects on other parts of the biosphere are

harder to quantify, but they could have been important. It would be very surprising if light-skinned people would be the only species to be so strongly damaged by increased UV-B radiation.

Although the ozone layer may thus be recovering, a recent study by Shindell et al. (1998) indicates that as a result of the cooling of the stratosphere due to increasing CO₂ levels, it may be possible that for another two decades stratospheric ozone in both hemispheres may further decrease, an effect that could be especially pronounced over the Arctic, maybe leading there to ozone columns similarly low as over Antarctica. In fact, Waibel et al. (1999) point to the possibility that, because of cooling of the stratosphere by increasing CO₂, even by the third quarter of 2000 severe ozone depletion may still occur.

1.3 Conclusions

Humankind is having a considerable influence on the condition in the atmosphere, even in areas that are very far removed from the pollution sources. Most surprisingly and unexpectedly, over Antarctica during September–October, enormous damage is done to the ozone layer due to a remarkable combination of feedbacks: radiative cooling, giving very low winter and springtime temperatures, and the presence of chlorine gases in the stratosphere at concentrations about six times greater than that of the natural background provided by CH₃Cl. The cold temperatures promote the formation of solid or supercooled liquid polar stratospheric cloud particles consisting of a mixture of H₂SO₄, HNO₃, and H₂O, on whose surfaces, or within which, reactions take place that convert HCl and ClONO₂ (which do not react with ozone) to highly reactive radicals Cl and ClO. The latter rapidly remove ozone from the lower stratosphere by catalytic reactions. Nobody predicted this course of events. In fact, until the discovery of the ozone hole, it was generally believed that ozone at high latitudes could not be significantly affected at all by chemical processes and was only subjected to transport. How wrong we all were. Exactly in the part of the stratosphere the farthest away from the industrialized world, and exactly in that altitude region at which until about 1980 maximum concentrations of ozone had always been found, mainly during the month of September, all ozone is going to be destroyed for many more years to come, despite the international agreements that are now in place. This is due to a number of positive feedbacks. This ozone loss should be a warning. It can be difficult or impossible to predict precisely where the weak points in the environment are located. It is therefore important to watch even for seemingly unlikely chains of positive feedbacks leading to major environmental impacts. Examples of potential instabilities were discussed at this workshop, including abrupt climate changes and a weakening of the Atlantic deep-water formation.

1.4 Epilog: And Things Could Have Been Much Worse

Gradually, if the studies by Shindell et al. (1998) and Waibel et al. (1999) turn out not to be valid, over a period of a century or so, stratospheric ozone should largely

recover to its natural state. However, it was a close call. Had Farman and his colleagues not persevered in making their measurements in the harsh Antarctic environment for all those years since the International Geophysical Year 1958/1959, the discovery of the ozone hole might have been substantially delayed, and there might have been far less urgency to reach international agreement on the phasing out of CFC production. There might thus have been a substantial risk that an ozone hole could also have developed in the higher latitudes of the Northern Hemisphere.

Furthermore, whereas the establishment of an instability in the O_3/ClO_x system requires chlorine activation by heterogeneous reactions on solid or in supercooled liquid particles, this is not required for inorganic bromine, which, because of gas-phase photochemical reactions, is normally largely present in its activated forms Br and BrO. This makes bromine almost 100 times more dangerous for ozone than chlorine on an atom-to-atom basis. This brings up the nightmarish thought that if the chemical industry had developed organobromine compounds instead of the CFCs – or alternatively, if chlorine chemistry had behaved more like that of bromine – then without any preparedness, we would have been faced with a catastrophic ozone hole everywhere and in all seasons during the 1970s, probably before atmospheric chemists had developed the necessary knowledge to identify the problem and the appropriate techniques for the necessary critical measurements. Noting that nobody had worried about the atmospheric consequences of the release of Cl or Br before 1974, I can only conclude that we have been extremely lucky. This shows that we should always be on our guard for the potential consequences of the release of new products into the environment. Continued surveillance of the composition of the stratosphere, therefore, remains a matter of high priority for many years to come.

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